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(54) Nonaqueous secondary battery.

(57) A nonaqueous secondary battery comprising a positive electrode active material, a negative electrode active material, and a lithium salt is disclosed, in which the negative electrode active material contains (1) a compound capable of intercalating and deintercalating lithium comprising an atom of the group IIIB, IVB or VB of the periodic table, (2) an amorphous compound containing at least two atoms selected from the elements of the groups IIIB, IVB, and VB of the periodic table, (3) a compound capable of intercalating and deintercalating lithium containing at least one of the atoms of the group IIIB, IVB, and VB of the periodic table and fluorine, or (4) a compound of the metal of the group IIIB, IVB or VB of the periodic table, Zn, or Mg which is capable of intercalating and deintercalating lithium. The nonaqueous secondary battery of the invention exhibits improved charge and discharge characteristics and improved safety.

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FIELD OF THE INVENTION

This invention relates to a nonaqueous secondary battery having improved charge and discharge cycle characteristics and improved safety.

BACKGROUND OF THE INVENTION

Negative electrode active materials for nonaqueous secondary batteries typically include metallic lithium and lithium alloys. The problem associated with these active materials is that metallic lithium grows dendritically during charging and discharging to cause an internal short circuit, involving a danger of ignition because of high activity of the dendritical metal per se. To solve the problem, a calcined carbonaceous material capable of intercalating and deintercalating lithium has recently been put to practical use. However, since the carbonaceous material has electrical conductivity by itself, metallic lithium is sometimes precipitated on the carbonaceous material at the time of an overcharge or a rapid charge. It eventually follows that lithium grows dendritically thereon. This problem has been dealt with by altering a charger or reducing the amount of the positive electrode active material to prevent an overcharge. Where the latter solution is adopted, however, the limited amount of the active material leads to a limited discharge capacity. Further, the carbonaceous material has a relatively low density and therefore a low capacity per unit volume. Thus, the discharge capacity is limited by both the amount of the active material and the capacity per unit volume.

In addition to metallic lithium, lithium alloys and the above-mentioned carbonaceous material, negative electrode active materials so far proposed include TiS_2 and $LiTiS_2$ which are capable of intercalating and deintercalating lithium (U.S. Patent 3,983,476); transition metal oxides having a rutile structure, such as WO_2 (U.S. Patent 4,198,476), spinel compounds, such as $Li_xFe(Fe_2)O_4$ (JP-A-58-220362, the term "JP-A" as used herein means an "unexamined published Japanese patent application"); a electrochemically synthesized lithium compound of Fe_2O_3 (U.S. Patent 4,464,447); a lithium compound of Fe_2O_3 (JP-A-3-112070); Nb_2O_5 (JP-B-62-59412 (the term "JP-B" as used herein means an "examined published Japanese patent application") and JP-A-2-82447); FeO, Fe_2O_3, Fe_3O_4, CoO, Co_2O_3, and Co_3O_4 (JP-A-3-291862); amorphous V_2O_5 (JP-A-4-223061); and transition metal oxides having their basic crystal structure changed by intercalation of a lithium ion (EP 567149). Any of these known compounds has a high oxidation-reduction potential, failing to provide a nonaqueous secondary battery having a discharge potential as high as 3 V and a high capacity.

SnO_2 or Sn compounds are used as an active material of lithium batteries as in $Li_{1.03}Co_{0.95}Sn_{0.04}O_2$ as a secondary battery positive electrode active material (EP 88-106301); SnO_2-added V_2O_5 as a secondary battery positive electrode active material (JP-A-2-158056); SnO_2-added α-Fe_2O_3 (preferred SnO_2 content: 0.5 to 10 mol%) as a secondary battery negative electrode active material (JP-A-62-219465); and SnO_2 as a primary battery positive electrode active material (Denki Kagaku oyobi Kogyo Butsuri Kagaku, Vol. 46, No. 7, p. 407 (1978)). With reference to the use of SnO_2 or Sn compounds as an electrochromic electrode, it is known that SnO_2 is capable of reversible intercalation of an Li ion (see Journal of Electrochemical Society, Vol. 140, No. 5, L81 (1993) and that a film comprising InO_2 doped with 8 mol% of Sn (i.e., ITO) is capable of reversible intercalation of an Li ion (see Solid State Ionics, Vols. 28-30, p. 1733 (1988)). However, the electrode useful in an electrochromic system should be transparent, the active material is used in the form of a thin film formed by, for example, vacuum evaporation, and the electrode usually works at a considerably low current differing from the practical range of batteries. For example, Solid State Ionics, supra, shows a working current of 1 μA to 30 $\mu A/cm^2$ as an experimental example.

Known positive electrode active materials include spinel compounds disclosed in JP-B-4-30146 and cobalt oxide disclosed in JP-B-63-59507.

It is possible to combine these positive electrode active materials with an oxide mainly comprising Sn as a negative electrode active material to provide a nonaqueous secondary battery having a high discharge potential, a high capacity, improved charge and discharge cycle characteristics, and increased safety. Yet, the charge and discharge cycle characteristics are still unsatisfactory as described above, and it has been keenly demanded to further improve charge and discharge cycle characteristics.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a nonaqueous secondary battery having improved charge and discharge cycle characteristics, a high discharge potential, a high discharge capacity, and increased safety.